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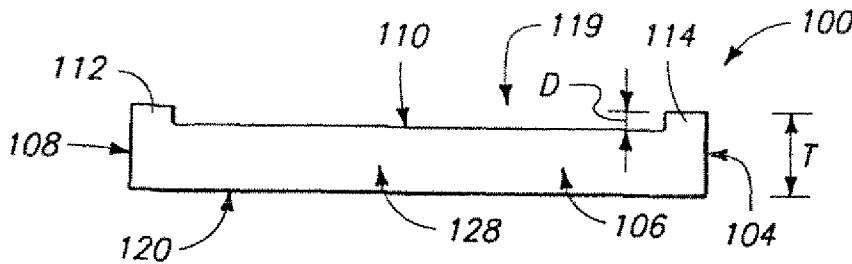
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(54) Title: **MICROELECTRONIC LID DESIGNS, HEAT SPREADER DESIGNS, AND SEMICONDUCTOR PACKAGES**



(57) Abstract: The invention encompasses microelectronic package lids, heat spreaders, and semiconductor packages comprising microelectronic lids or heat spreaders. In particular aspects of the present invention, a microelectronic lid comprises a material having a rectangular peripheral shape that defines 4 peripheral sides. Further, the lid has projecting peripheral rails along less than all of the peripheral edge. For instance, the lid can have projecting peripheral rails along only 2 of the sides. Alternatively, such microelectronic lid can be described as comprising a generally rectangular shape defining four peripheral edges, with two of the edges having a greater thickness than the other two edges.

**WO 02/41394 A2**

Microelectronic Lid Designs, Heat Spreader Designs, and Semiconductor Packages**TECHNICAL FIELD**

This invention pertains to microelectronic lid designs, heat spreader designs, and  
5 semiconductor packaging.

**BACKGROUND OF THE INVENTION**

Modern semiconductor device packaging typically involves provision of a  
microelectronic lid over a semiconductor die (also referred to as a chip) to protect the die during  
10 transport. The microelectronic lid can be thermally conductive with the die so that heat generated  
from the die is dispersed into the lid. Accordingly, the lid can function as a heat spreader in  
addition to functioning as a protective cover for the die.

A prior art semiconductor package is described with reference to Figs. 1-4. Referring  
initially to Fig. 1, the package comprises a base 10 and a lid 30, which are initially provided as  
15 separate pieces. Base 10 can comprise a substrate 12, which can be a circuit-retaining  
construction, such as, for example, a circuit board. A semiconductor chip 14 is provided in  
electrical connection with the circuit of circuit-retaining construction 12, and can, for example,  
be connected to such circuit through solder bead electrical interconnects (not visible in the view  
of Fig. 1). A sealant material 16 is provided around an outer periphery of circuit-retaining  
20 construction 12, and can comprise, for example, an epoxy. The surface of base 10 that is shown  
in Fig. 1 will ultimately be an inner surface in a package construction formed with lid 30.

Referring next to lid 30, such comprises a recessed surface 32 surrounded by a non-  
recessed peripheral portion 34. Lid 30 also comprises a surface 36 that is in opposing  
relationship to surface 32, and accordingly that is a hidden underside of lid 30 in the view of Fig.  
25 1. The surface 32 of lid 30 will ultimately be an inner surface of the lid in a package formed with  
lid 30 and base 10, and the surface 36 will be an outer surface of such package.

Fig. 2 shows a top view of a package 40 comprising lid 30 and base 10. A process step  
in formation of package 40 is to invert lid 30 from the configuration shown in Fig. 1, and to press  
the lid over base 10. Lid 30 is sealed to base 10 by sealing peripheral portion 34 of lid 30 to the  
30 base with sealant material 16.

Fig. 3 shows a cross-sectional view through the package 40 of Fig. 2, and illustrates lid  
30 joined with base 10. Also visible in Fig. 3 are electrical interconnects 42 extending  
downwardly from chip 14 to electrically connect the chip with circuitry (not shown) retained in  
substrate 12. Additionally, Fig. 3 shows a thermally conductive interface material 44 provided  
35 on chip 14 and thermally connecting lid 30 with chip 14 to allow heat dispersion from chip 14  
into lid 30. If material 44 were not present, or were replaced with a non-thermally conductive  
material, lid 30 would simply be a microelectronic lid. However, if material 44 is a thermally

conductive material, lid 30 functions as a heat spreader, with the term heat spreader understood to indicate a construction that primarily spreads heat in two dimensions, rather than in three dimensions.

Fig. 4 illustrates the package 40 of Fig. 3 attached to a heat sink 50 through a thermally 5 conductive interface material 52. Material 52 can comprise, for example, GELVET<sup>TM</sup>, which is commercially available from Honeywell International, Inc. Heat sink 50 can comprise, for example, aluminum having a shape which incorporates numerous projecting fins and/or posts. The heat sink 50 is distinguished from a heat spreader, in that heat sink 50 disperses heat in three dimensions, rather than two.

10 It can be problematic and costly to fabricate a lid having the complexity of lid 30. Accordingly, it would be desired to develop improved microelectronic lid designs.

### **SUMMARY OF THE INVENTION**

The invention encompasses microelectronic package lids, heat spreaders, and 15 semiconductor packages comprising microelectronic lids or heat spreaders. In particular aspects of the present invention, a microelectronic lid comprises a material having a rectangular peripheral shape that defines 4 peripheral sides. Further, the lid has projecting peripheral rails along less than all of the peripheral edge. For instance, the lid can have projecting peripheral rails along only 2 of the sides. Alternatively, such microelectronic lid can be described as comprising a generally rectangular shape defining 4 peripheral edges, with 2 of the edges having 20 a greater thickness than the other 2 edges.

The invention also encompasses heat spreaders having the above-described shapes of the microelectronic lids, and comprising materials with a thermal conductivity of at least 100 watts/meter-kelvin, preferably at least 150 watts/meter-kelvin, and more preferably greater than 25 200 watts/meter-kelvin. In particular embodiments, the heat spreaders can comprise, consist or, or consist essentially of copper, and can have a thermal conductivity of about 350 watts/meter-Kelvin. In other embodiments, the heat spreaders can comprise, consist of, or consist essentially of aluminum, and can have a thermal conductivity of about 220 watts/meter-kelvin.

30 **BRIEF DESCRIPTION OF THE DRAWINGS**

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

Fig. 1 is a diagrammatic view of a microelectronic package at a preliminary step of a prior art method for forming a package, and is shown comprising a lid which is separate from a base. The lid is shown in a bottom view, and the base is shown in top view.

35 Fig. 2 is a view of a package comprising the lid and base of Fig. 1, and is shown in top view.

Fig. 3 is a view of the Fig. 2 package shown along the line 3-3.

Fig. 4 is a view of the Fig. 2 package shown along the cross sectional view of Fig. 3, and shown at a processing step subsequent to that of Fig. 3.

Fig. 5 is a diagrammatic bottom view of a microelectronic lid, or alternatively a heat spreader, encompassed by the present invention.

Fig. 6 is a side view of the Fig. 5 lid.

Fig. 7 is a view of the Fig. 5 lid in combination with a base, and shown at a preliminary step of forming a microelectronic package encompassed by the present invention. The base of Fig. 7 is shown in top view, while the lid is shown in bottom view.

Fig. 8 is a top view of a package assembled utilizing the lid and base of Fig. 7.

Fig. 9 is a cross-sectional view of the package of Fig. 8 shown along the line 9-9.

Fig. 10 is a cross-sectional view of the Fig. 8 package shown along the line 9-9, and shown at a processing step subsequent to that of Fig. 9.

Fig. 11 is a sideview of the Fig. 8 package.

Fig. 12 is a sideview of the Fig. 8 package, and shown in accordance with an embodiment of the present invention different than that of Fig. 11.

Fig. 13 is an isometric view of a piece of lid stock at a preliminary step of forming lids in accordance with a method of the present invention.

Fig. 14 is an isometric view of the lid stock of Fig. 13 shown at a processing step subsequent to that of Fig. 13.

#### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

A microelectronic lid, or alternatively a heat sink, encompassed by the present invention is described with reference to Fig. 5, and is shown generally as a lid 100. Lid 100 comprises a generally rectangular shape (although other shapes are encompassed by the present invention, with such other shapes including, for example, circular, triangular, pentagonal, or other polygonal shapes). Lid 100 comprises a periphery defined by the four edges 102, 104, 106 and 108. Lid 100 also comprises a recessed surface 110, which is coextensive with the surface of edges 102 and 106; and raised rails 112 and 114 which extend along edges 108 and 104. Additionally, lid 100 comprises a surface 120 (not visible in the view of Fig. 5) which is in opposing relation to surface 110.

A difference between the lid 100 of Fig. 5 and the prior art lid 30 (shown in Fig. 1) is in lid 100 having raised portions (112 and 114) extending along only a part of the periphery of the lid. In contrast, the prior art lid 30 has a raised portion (34) extending along its entire periphery.

In the shown embodiment, lid 100 comprises a rectangular shape, and the raised peripheral portions are along two opposing sides (104 and 108) of the peripheral shape, while the remaining two sides (102 and 106) do not have raised portions extending along the predominate

extent of such edges. In fact, the only raised portions associated with edges 102 and 106 are the terminal ends of raised portions 112 and 114, with such ends being the regions of portions 112 and 114 that contact edges 102 and 106. Such terminal portions of rails 112 and 114 are identified in Fig. 5 by the label 115. Accordingly, edge 102 has an expanse 126 extending along the edge between terminal ends 115 of rails 112 and 114, and such expanse 126 is not raised relative to surface 110. Similarly, edge 106 has an expanse 128 extending between terminal ends 115 which is not raised relative to surface 110.

Fig. 6 shows a side view of lid 100 along the side 106. Such side view illustrates the relationship of rails 112 and 114 relative to surface 110, and further shows expanse 128 extending between rails 112 and 114. Rails 112 and 114 define a groove 119 extending therebetween.

Exemplary dimensions of the lid 100 of Figs. 5 and 6 are a width "W" of about  $35 \pm 0.35$  millimeters; a length "L" of about  $35 \pm 0.35$  millimeters, and a thickness "T" of about  $4.6 \pm 0.05$  millimeters. Further, groove 119 can have a depth "D" of about  $0.6 \pm 0.025$  millimeters.

Referring next to Fig. 7, lid 100 is shown adjacent a base 150, which is ultimately to be capped by lid 100 to form a package. Base 150 comprises four peripheral edges (151, 153, 155 and 157), and is similar to the base 10 of Fig. 1 in that it comprises a die 14 over a substrate 12. Further, base 150 comprises a sealant 16 provided along peripheral edges of the substrate. However, a difference between base 150 of Fig. 7 and base 10 is that the sealant 16 is provided along only two of the peripheral edges of substrate 12 of base 150, rather than along the four peripheral edges as was done with base 10. Sealant 16 is provided along the two peripheral edges of the substrate 12 of base 150 that will ultimately contact raised edges associated with lid 100.

In a processing step subsequent to that of Fig. 7, lid 100 is placed over base 150, and rails 112 and 114 are sealed against the base with sealant 16 to form a package. Such package is shown in Fig. 8 as a package 200, and specifically is shown in top view, with surface 120 of lid 100 being visible.

Referring next to Fig. 9, package 200 is shown in cross-sectional view along the line 9-9 of Fig. 8. Such cross-sectional view shows solder beads 42 connecting die 14 with substrate 12. Also, the cross-sectional view shows a layer 202 formed between die 14 and lid 100. Layer 202 can comprise, for example, a thermally conductive material. If layer 202 comprises a thermally conductive material, then lid 100 can function as a heat spreader to dissipate heat generated by die 14. In alternative embodiments, layer 202 can be omitted, or can be replaced with a non-thermally conductive material. In either of such alternative embodiments, lid 100 will function as a microelectronic lid to protect die 14, but will generally not effectively dissipate heat from die 14, and accordingly will not be utilized as a heat spreader.

If lid 100 is utilized as a heat spreader, it preferably comprises a material with a thermal conductivity of at least 100 watts/meter-kelvin, and more perfectly at least 150 watts/meter-kelvin. In particular embodiments, lid 100 can comprise a material having a thermal conductivity in excess of 200 watts/meter-kelvin, such as, for example, copper or aluminum. In 5 embodiments in which lid 100 comprises a metallic material, the lid can be nickel-plated. For instance, if lid 100 comprises copper or aluminum, it can be provided with a nickel-plating having a thickness of at least about 3 microns. The nickel plating can protect the underlying lid material from corrosion, and further can provide a reproducible surface for adherence to one or more thermal interface materials, as well as for adherence to epoxy.

10 Referring next to Fig. 10, package 200 is illustrated after formation of a heat sink 50 over the package, and a thermal interface 52 connecting heat sink 50 with package 200. Heat sink 50 and thermal interface 52 can comprise, for example, the materials described above with reference to the prior art construction of Fig. 4.

15 Referring next to Fig. 11, the package 200 of Fig. 8 is shown in a side view. The chip (14) is not shown in the side view of Fig. 11 to simplify the drawing, although it is to be understood that chip 14 would be in the center of package 200 as illustrated by, for example, Fig. 9. The view of Fig. 11 shows that there is a gap 250 at the end of package 200 corresponding to a space between rails 112 and 114. Such gap will typically be narrow, and in particular embodiments of the present invention can be left unfilled. However, if it is desired to fill gap 20 250 to prevent dirt or other contaminants from penetrating between lid 100 and substrate 150, such can be accomplished by providing a filler material within the gap. Such is illustrated in Fig. 12, wherein gap 250 is filled with a filler material 260. Filler material 260 can comprise, for example, epoxy. Filler material 260 can be provided after formation of package 200 by applying the filler material into gap 250. Alternatively, filler material 250 can be provided before 25 formation of package 200 at, for example, the processing step of Fig. 7, by providing the filler material at edges 151 and 153 of substrate 150.

30 The lid 100 of the present invention can be advantageous relative to prior art lids (such as, for example, the lid 30 of Fig. 1) in that lid 100 can be simpler to manufacture than the prior art lids. Lid 100 can be formed by, for example, the processing of Figs. 13 and 14. Referring initially to Fig. 13, a bar 300 of lid stock is provided. The bar comprises dimensions "A", "X", and "Y". Dimension "X" corresponds to a width along edge 106 of a finished lid 100 (Figs. 5 and 6), and dimension "Y" corresponds to a thickness of rails 112 and 114 of a finished lid 100. The dimension "A" is preferably longer than several integral lengths of edge 108 of a finished lid 100.

35 Referring next to Fig. 14, bar 300 is machined to form a groove 302 extending along a surface of the bar. Groove 302 defines rails 112 and 114 extending along edges of the lid stock. The stock can subsequently be cut along dashed lines 304 and 306 to define separated lids 100,

400 and 500. The lids separated lids can subsequently be subjected to electroplating if a metal plating is desired over the material of the lids.

Although Figs. 13 and 14 illustrate a process wherein a lid stock bar 300 is machined to form groove 302, it is to be understood that the invention encompasses alternative processing 5 wherein the grooved material of Fig. 14 is formed by extruding a lid material into the shown shape.

CLAIMS

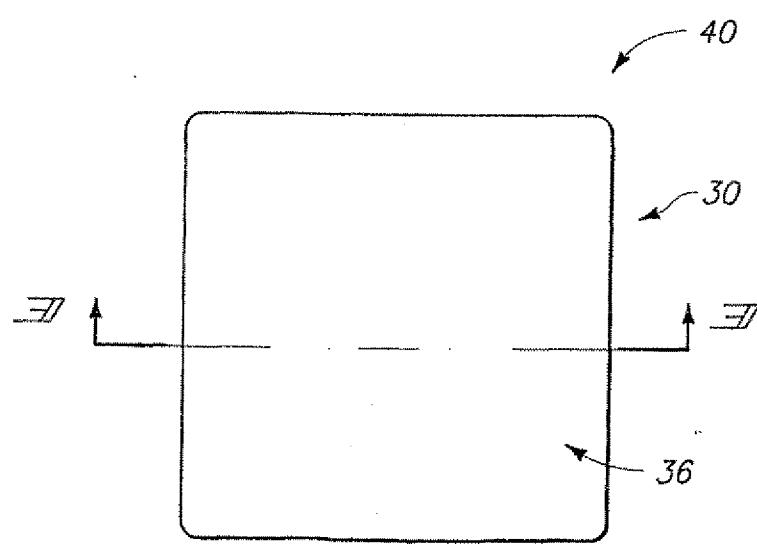
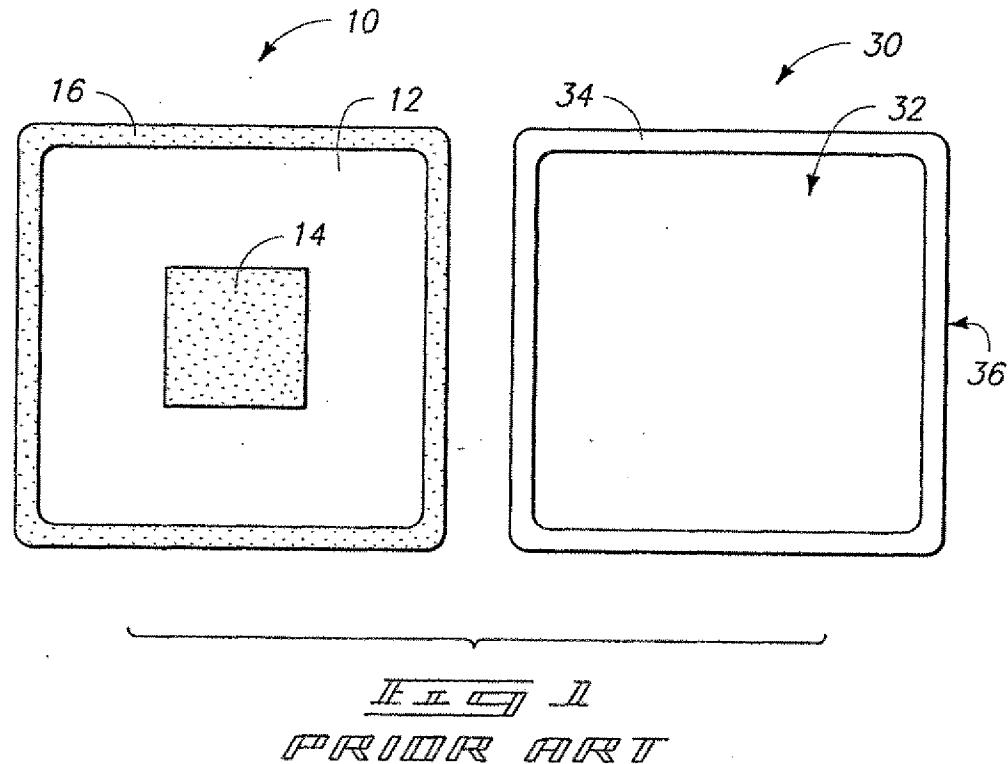
1. A microelectronic lid, comprising:
  - 5 a lid material having a shape and a peripheral edge surrounding the shape;
  - a surface surrounded by the peripheral edge; and
  - a rail which extends along only a portion of the peripheral edge and which is elevationally raised relative to the surface.
2. The microelectronic lid of claim 1 wherein the shape is a rectangular shape defining
  - 10 four peripheral sides of the peripheral edge, and wherein the rail extends along two of the peripheral sides, while at least a predominate portion of the remaining two sides does not have the rail extending there-along.
3. The microelectronic lid of claim 2 wherein the two of the peripheral sides along which
  - 15 the rail extends are in opposing relation to one another.
4. The microelectronic lid of claim 2 wherein the rectangular shape is a square shape.
5. The microelectronic lid of claim 1 incorporated within a microelectronic package, the
  - 20 package comprising:
    - a base;
    - a chip supported by the base; and
    - the microelectronic lid over the chip; the chip accordingly being packaged between the microelectronic lid and the base.
- 25 6. The microelectronic package of claim 5 wherein the microelectronic lid has a thermal conductivity of at least about 100 watts/meter-Kelvin; and further comprising a thermally conductive connection between the microelectronic lid and the chip.
- 30 7. The microelectronic lid of claim 6 wherein the microelectronic lid has a thermal conductivity of at least about 150 watts/meter-Kelvin.
8. The microelectronic lid of claim 6 wherein the microelectronic lid has a thermal conductivity of at least about 200 watts/meter-Kelvin.
- 35 9. The microelectronic lid of claim 6 wherein the microelectronic lid comprises copper.

10. The microelectronic lid of claim 6 wherein the microelectronic lid comprises aluminum.
11. The microelectronic lid of claim 1 comprising copper.  
5
12. The microelectronic lid of claim 1 consisting essentially of copper.
13. The microelectronic lid of claim 1 consisting of copper.
- 10 14. The microelectronic lid of claim 1 consisting essentially of metal-plated copper.
15. The microelectronic lid of claim 1 consisting of metal-plated copper.
16. The microelectronic lid of claim 1 consisting essentially of nickel-plated copper.  
15
17. The microelectronic lid of claim 1 consisting of nickel-plated copper.
18. The microelectronic lid of claim 1 comprising aluminum.
- 20 19. The microelectronic lid of claim 1 consisting essentially of aluminum.
20. The microelectronic lid of claim 1 consisting of aluminum.
21. The microelectronic lid of claim 1 consisting essentially of metal-plated aluminum.  
25
22. The microelectronic lid of claim 1 consisting of metal-plated aluminum.
23. The microelectronic lid of claim 1 consisting essentially of nickel-plated aluminum.
- 30 24. The microelectronic lid of claim 1 consisting of nickel-plated aluminum.
25. A method of forming a plurality of microelectronic lids, comprising:  
providing a bar of lid stock;  
forming a groove along a side of the bar; and  
35 after forming the groove, cutting the bar into a plurality of separated microelectronic lids.

26. The method of claim 25 wherein the bar comprises aluminum.
27. The method of claim 25 wherein the bar comprises copper.
- 5 28. The method of claim 25 wherein the bar comprises a first metallic material, and further comprising electroplating the separated microelectronic lids with a second metallic material.
29. The method of claim 25 wherein the bar comprises aluminum or copper, and further comprising electroplating the separated microelectronic lids with nickel.
- 10 30. The method of claim 25 further comprising incorporating at least one of the microelectronic lids into a microelectronic package, the incorporating comprising:
  - providing a chip supported by a base; and
  - adhering the microelectronic lid to the base and over the chip; the chip accordingly being packaged between the microelectronic lid and the base.
- 15 31. A method of forming a plurality of microelectronic lids, comprising:
  - extruding a lid stock material into a shape of a bar having a side, and a groove extending along the side; and
  - 20 after extruding the material, cutting the bar into a plurality of separated microelectronic lids.
32. The method of claim 31 wherein the lid stock material comprises aluminum.
- 25 33. The method of claim 31 wherein the lid stock material comprises copper.
34. The method of claim 31 wherein the lid stock material comprises a first metallic material, and further comprising electroplating the separated microelectronic lids with a second metallic material.
- 30 35. The method of claim 31 wherein the lid stock material comprises aluminum or copper, and further comprising electroplating the separated microelectronic lids with nickel.

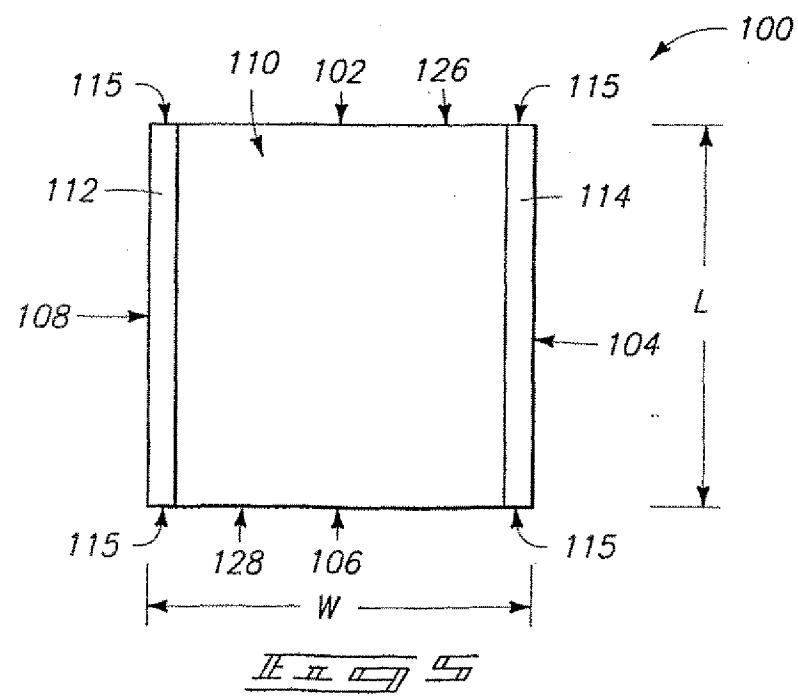
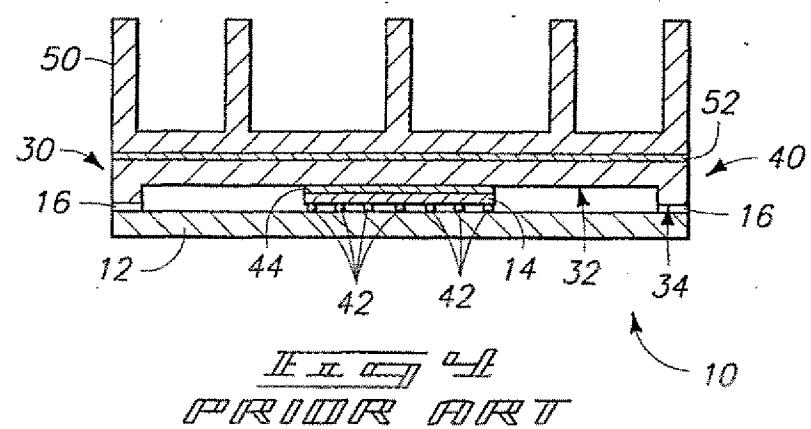
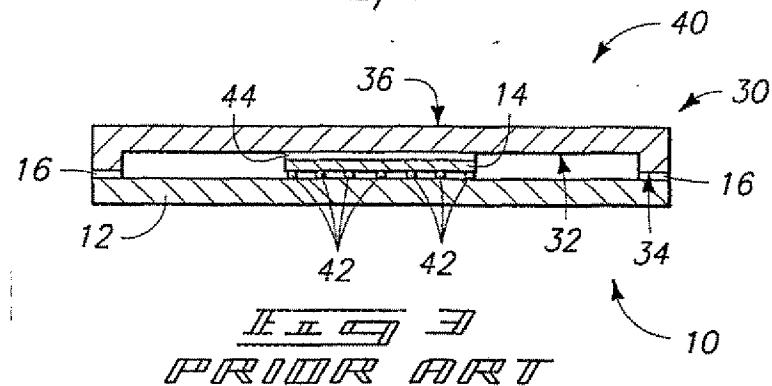
36. The method of claim 31 further comprising incorporating at least one of the microelectronic lids into a microelectronic package, the incorporating comprising:  
providing a chip supported by a base; and  
adhering the microelectronic lid to the base and over the chip; the chip accordingly being packaged between the microelectronic lid and the base.

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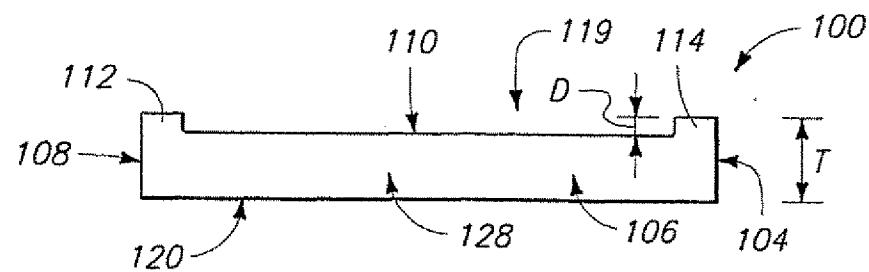
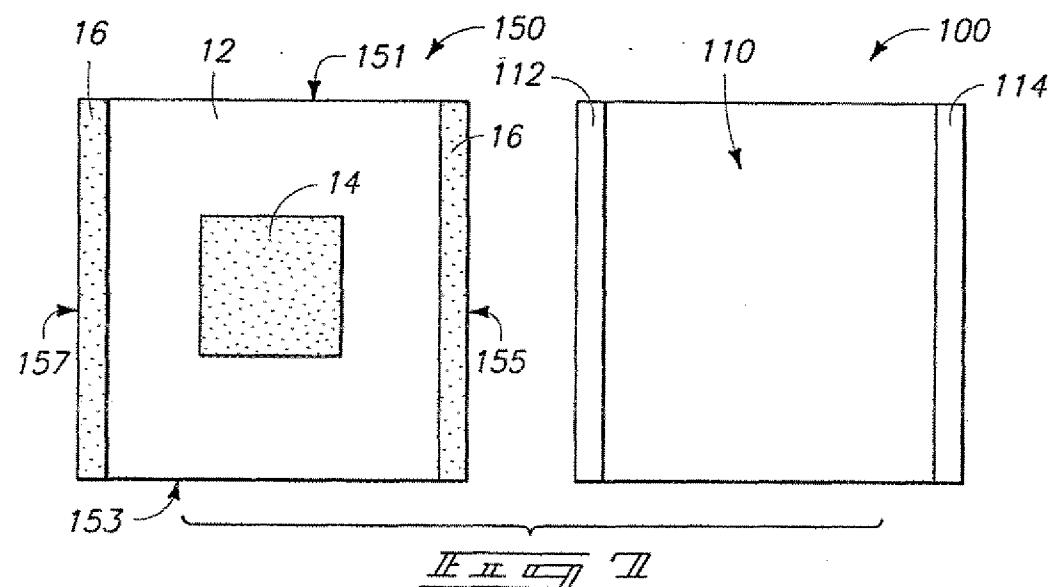
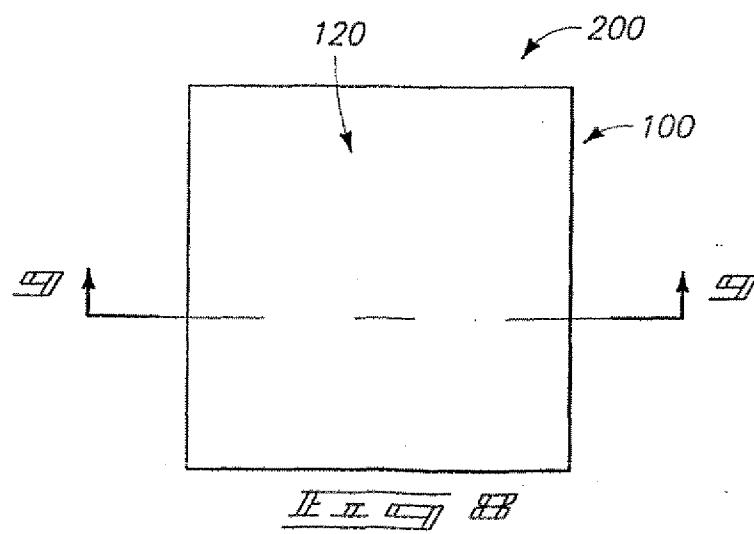


Ex. 2  
PRIOR ART

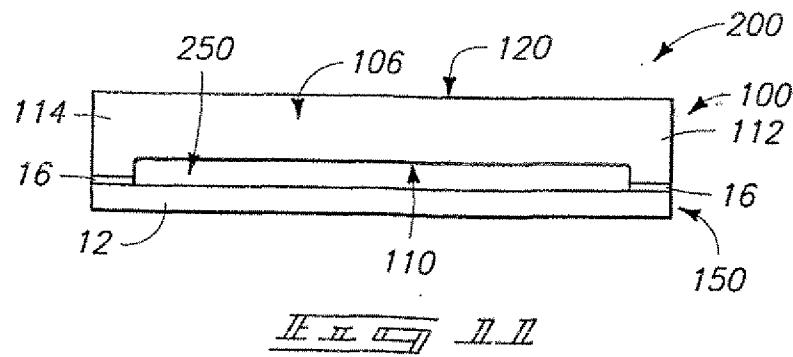
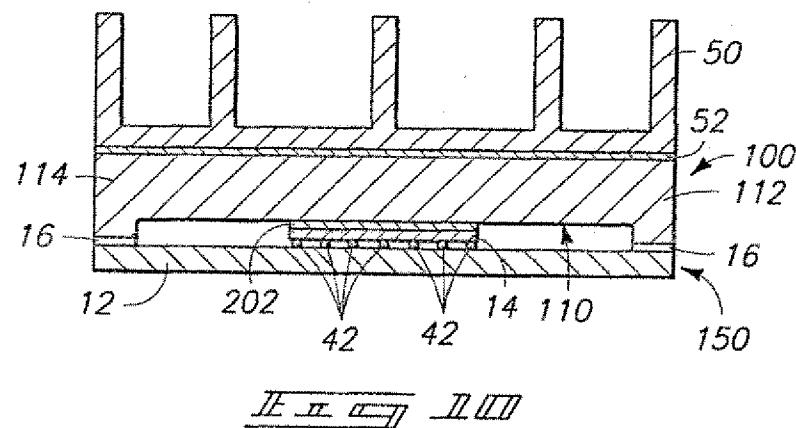
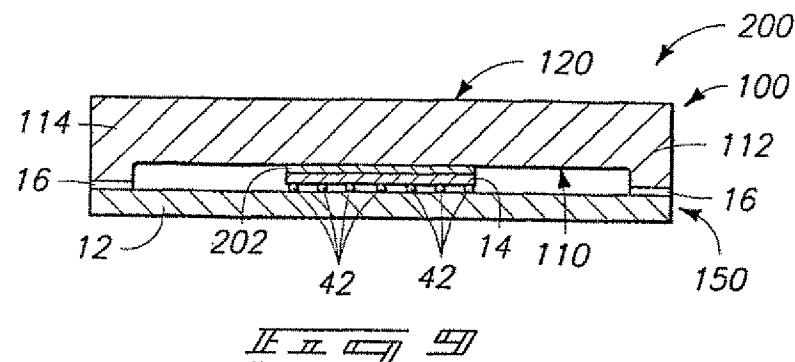
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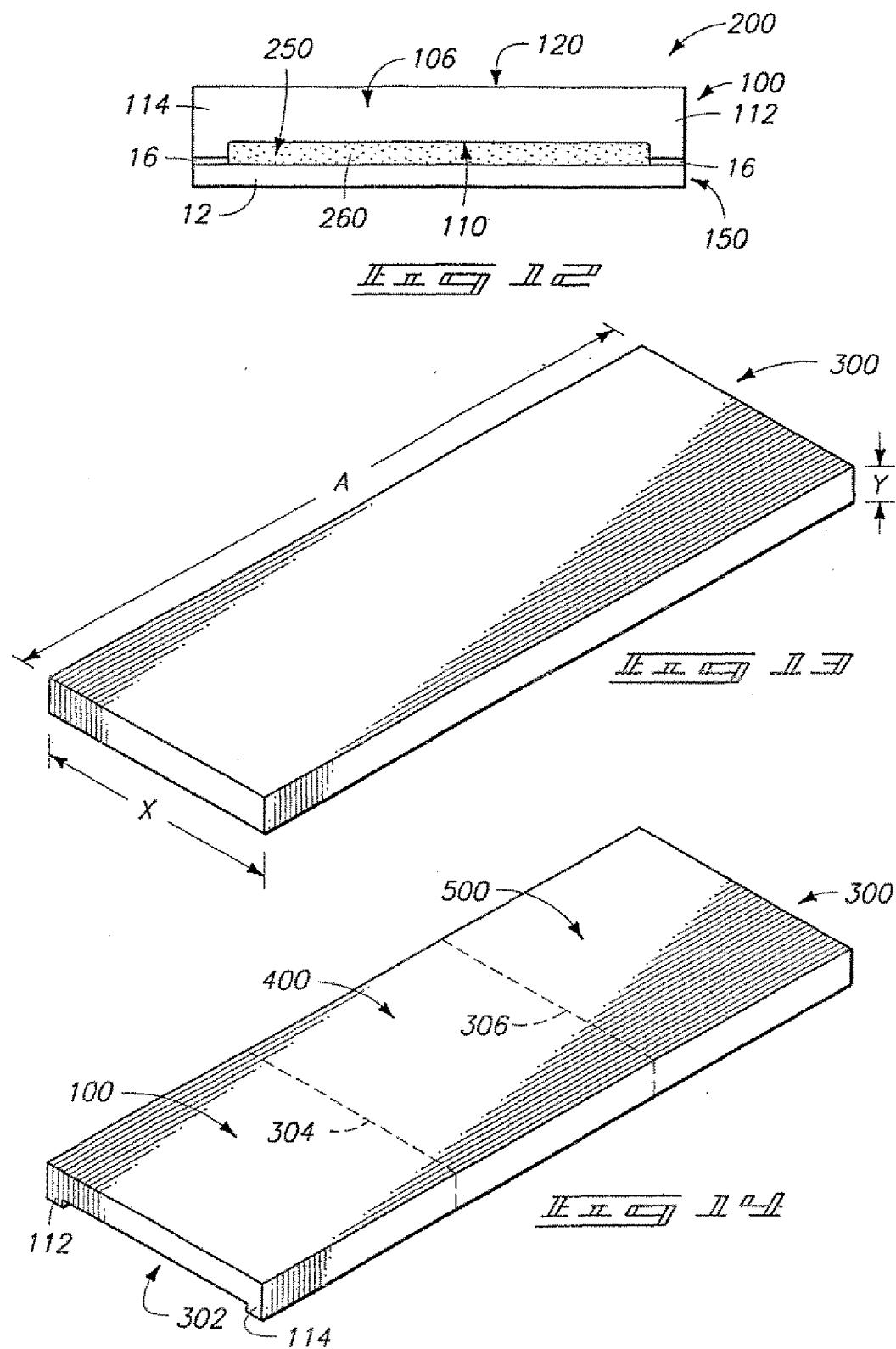
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FIGURE 5FIGURE 7FIGURE 8

4/5



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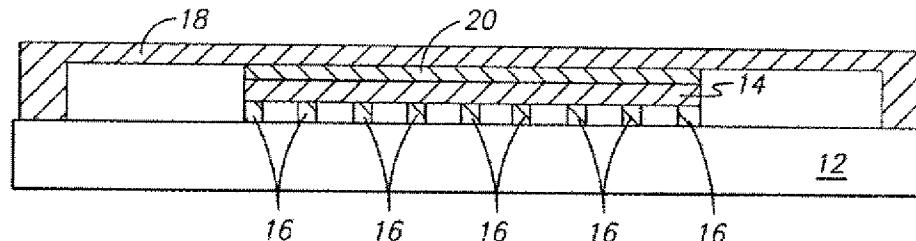
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— with amended claims

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(54) Title: THERMAL INTERFACE MATERIALS; AND COMPOSITIONS COMPRISING INDIUM AND ZINC

**WO 03/064713 A1**



(57) **Abstract:** The invention includes a semiconductor package (10) which comprises a semiconductor substrate (14) and a heat spreader (18). A thermal interface material (20) thermally connects the substrate to the heat spreader (18). The thermal interface material (20) consists essentially of In, Zn, and one or more elements selected from the group consisting of Mg, Ca, Nb, Ta, B, Al, Ce, Ti and Zr. The invention also includes a composition consisting essentially of In and Zn. The Zn concentration within the composition is from about 0.5 weight% to about 3 weight%.

## Thermal Interface Materials, and Compositions Comprising Indium and Zinc

### TECHNICAL FIELD

**[0001]** The invention pertains to thermal interface materials, and in particular applications pertains to thermal interface materials comprising indium and zinc. The invention also pertains to compositions comprising indium and zinc. The invention can further pertain to methods of forming thermal interface materials.

### BACKGROUND OF THE INVENTION

**[0002]** Thermal interface materials (TIMs) have numerous applications for conducting heat to and/or from electrical components. One application of TIMs is to conduct heat away from semiconductor devices during operation of integrated circuitry associated with the devices.

**[0003]** It is desired to develop compositions which can be utilized for TIMs. It is also desired that the TIMs have high thermal conductivity for present and future semiconductor packages. It is further desired that the TIMs be suitable for utilization between a semiconductor device and a lid (heat spreader). Additionally, it is desired that the TIMs be suitable for bonding to a variety of surfaces and have a low modulus with high strength.

### SUMMARY OF THE INVENTION

**[0004]** In one aspect, the invention includes a semiconductor package. The package comprises a semiconductor substrate and a heat spreader proximate the substrate. A thermal interface material thermally connects the substrate to

the heat spreader. The thermal interface material consists essentially of In and Zn. Alternatively, the thermal interface material can consist essentially of In, Zn and one or more elements selected from the group consisting of Mg, Ca, Nb, Ta, B, Al, Ce, Ti and Zr. The Zn concentration within the material can be, for example, from about 0.5 weight% to about 3 weight%.

**[0005]** In one aspect, the invention includes a composition consisting essentially of In and Zn. The Zn concentration within the composition is from about 0.5 weight% to about 3 weight%. The invention also includes a composition consisting essentially of In, Zn and one or more of Mg, Ca, Nb, Ta, B, Al, Ce, Ti and Zr.

#### BRIEF DESCRIPTION OF THE DRAWING

**[0006]** Preferred embodiments of the invention are described below with reference to the accompanying drawing. The drawing shows a diagrammatic cross-sectional view of a semiconductor package illustrating an exemplary aspect of the invention.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0007]** A composition formed in accordance with aspects of the present invention can be used to create all or part of a thermal interface material between a heat source and a heat sink, and/or a heat spreader. The thermal interface material can be considered to aid in transferring heat from one surface to another.

**[0008]** Compositions of the present invention can comprise, consist essentially of, or consist of In and Zn. Alternatively, compositions of the present

invention can comprise, consist essentially of, or consist of In, Zn and one or more elements selected from the group consisting of Mg, Ca, Nb, Ta, B, Al, Ce, Ti and Zr. The Zn in various exemplary compositions can be present to a concentration of less than or equal to 3 weight%, and in particular compositions can be present to a concentration of less than or equal to about 2.2 weight%. If one or more elements selected from the group consisting of Mg, Ca, Nb, Ta, B, Al, Ce, Ti and Zr are present, the total concentration of such one or more elements can be less than or equal to 1000 ppm. In particular applications, the total concentration of the one or more elements selected from the group consisting of Mg, Ca, Nb, Ta, B, Al, Ce, Ti and Zr is less than or equal to 500 ppm, or even less than or equal to 200 ppm.

**[0009]** The elements incorporated with Zn and In in various TIM compositions of the present invention can, in particular aspects of the invention, be considered dopants which aid in bonding the TIM to a silicon nitride surface associated with a semiconductor die. Accordingly, it can be desirable to utilize dopants which improve interaction of In-Zn with such surface. From thermodynamic data, Mg, Ca, Nb, Ta, B, Al, Ce, Ti and Zr are identified as having more stable nitrides than silicon. This would indicate that they would tend to react with the silicon nitride and form a good bond. Mg was chosen for the examples that follow, as it forms a reaction product with silicon and does not form intermetallics with In or Zn which could embrittle solders comprising In and Zn. In various applications of the invention, one or more other elements selected from the group consisting of Ca, Nb, Ta, B, Al, Ce, Ti and Zr can be used in addition to, or alternatively to, Mg.

**[0010]** A particular material utilized in aspects of the present invention can have a composition which comprises, consists essentially of, or consists of: (1) less than or equal to 1000 ppm Mg (the effect of Mg seems to degrade in 1000 ppm tests, with a Mg concentration of from about 200 ppm to about 500 ppm appearing to be optimal in particular applications); (2) less than or equal to 3 weight% Zn (a range of from about 0.5 weight% to about 2.2 weight% Zn appears to be typically desirable, with 1 weight% Zn being preferable in particular applications); and (3) indium. The concentration of Zn can be, for example, within a range of from greater than 0 weight% to less than or equal to 3 weight%; in some applications within a range of from greater than 0 weight% to less than or equal to 2.5 weight%; in further applications within a range of from greater than 0 weight% to less than or equal to 2 weight%; in yet further applications within a range of from greater than 0 weight% to less than or equal to 1.5 weight%; and in yet further applications within a range of from greater than 0 weight% to less than or equal to 1 weight%. In various particular applications the concentration of Zn can be chosen to form a eutectic alloy with the In of a composition.

**[0011]** In one aspect of the invention, an In-based alloy comprising about 1 weight% Zn and less than or equal to about 1000 ppm Mg is produced. The alloy is found to wet and bond (adhere) well to silicon nitride coated substrates. Various components of the alloy can impact physical characteristics of the alloy. For instance, indium can provide a low modulus and high thermal conductivity; zinc can improve the alloy's high temperature corrosion resistance; and magnesium can improve wetting and bonding to silicon nitride.

**[0012]** The alloy comprising In, Zn and Mg can be formed by (1) mixing pieces of In, Zn and Mg metals in a graphite crucible; (2) melting the metals at a temperature of from about 150°C to about 350°C to form a molten mixture; (3) pouring the molten mixture into a mold of a desired shape; and (4) cooling the mixture within the mold to form a solid mass of the alloy having the desired shape. The mass can subsequently be rolled or extruded by conventional metal-working techniques to form ribbon or wire suitable for, for example, utilization as solder.

**[0013]** In particular aspects of the invention, alloys of indium having greater than 95 weight% indium (such as alloys having greater than 98 weight% indium, and in some applications greater than 99 weight% indium) have thermal conductivities close to that of pure indium (82 W/m\*K). The alloys can consist of, or consist essentially of, for example, alloys of In and Zn which the concentration of Zn is from about 0.5 weight% to about 3 weight%. The indium of the alloys can enable the alloys to wet various surfaces. Wetting tests indicate that the alloys can have wetting forces approaching 500 microNewtons per millimeter on nickel. Zn can impart strength to the alloys, and can improve oxidation resistance of the alloys relative to the oxidation resistance of pure In.

**[0014]** Compositions of the present invention (such as In/Zn alloys) can be cast by conventional methods in air or under inert atmospheres. The metals can be melted together at, for example, about 450°C during the casting. Slabs or billets can be produced by the casting. The slabs or billets can be further processed to form ribbon or wire of the alloy compositions. The ribbon or wire can subsequently be utilized as a solder to form TIMs in particular applications.

**[0015]** A "dry interface" or one with no interface material present, will typically only have actual contact over about 1% of the interface area due to microscopic (surface roughness) and macroscopic (surface warpage or non-planarity) irregularities of the mating components. The remainder of the dry interface area contains an "air gap" across which it is difficult to conduct heat. Introducing a thermal interface material into this air gap area can improve the transport of thermal energy (heat) from one component to another.

**[0016]** Thermal resistance typically measures thermal interface material performance. Thermal resistance is the temperature drop across the interface times the interface area divided by the power flowing through the interface (reported in units of  $^{\circ}\text{C cm}^2/\text{W}$ ). The thermal resistance can be broken into three parts: (1) a contact resistance at the hot surface going into the interface material, (2) a bulk resistance due to thermal conduction through the interface material, and (3) a contact resistance at the interface material/cold surface junction. These are series resistances, which implies that all of them should be low to have a low overall thermal resistance.

**[0017]** The bulk thermal resistance is low when the interface material thermal conductivity is high. Accordingly, it is generally desired that an interface material have a high thermal conductivity. The thickness of an thermal interface material can also impact bulk thermal resistance, with thinner thermal interface materials having lower resistance than thicker materials. Accordingly, it is generally desired to use thin thermal interface materials.

**[0018]** The contact resistance between two contacting materials is preferably low. The contact resistance can be reduced if surfaces of the contacting materials interact with one another. For metallic materials, it is

desired to have good wetting behavior (spreading of one material relative to another). To improve reliability over time (as opposed to right after the joint is formed), it is desirable to have a fair degree of mutual solubility, intermetallic, and/or compound production, any of which can promote good adherence/bonding at the interface between contacting materials. Alloying additions or dopants can aid in achieving one or more of the above-described desired properties between contacting materials.

**Compositions of exemplary samples of material formed in accordance with  
aspects of the present invention**

**Example 1**

**[0019]** A composition consists essentially of, or consists of: In, 1 weight% Zn, and 250 ppm Mg.

**Example 2**

**[0020]** A composition consists essentially of, or consists of: In, 1 weight% Zn, and 500 ppm Mg.

**[0021]** Materials encompassed by various aspects of the present invention can be used as, for example, free standing solder (applied in ribbon, wire or preform shapes), solder paste, anodes, evaporation slugs, or solder components of polymer-solder hybrid interface materials. A schematic illustrating a use of a thermal interface material comprising a composition formed in accordance with an aspect of the present invention is shown in the Figure. More specifically, the Figure shows an assembled electronic package 10 comprising a base 12 supporting a semiconductor substrate 14. Substrate 14 can comprise, for example, a silicon die. Base 12 can comprise electrical connections (not shown) utilized for connecting circuitry (not shown) associated with substrate 14 to devices external of package 10. Substrate 14 can be connected to the electrical connections of base 12 through flip chip bumps 16.

**[0022]** A heat spreader 18 is proximate substrate 14, and in the shown embodiment forms a lid of package 10.

**[0023]** A thermal interface material 20 is provided between heat spreader 18 and substrate 14. The thermal interface material thermally connects substrate 14 with heat spreader 18, and in the shown embodiment is physically against both substrate 14 and heat spreader 18. It is to be understood, however, that other embodiments (not shown) can be utilized in which thermal interface material 20 is separated from one or both of substrate 14 and heat spreader 18 by other materials. Preferably such other materials are thermally conductive to enable thermal energy to be transferred across the materials to and from the thermal interface material.

**[0024]** Thermal interface material 20 can comprise any of the various compositions of the invention discussed above, including, for example, compositions consisting essentially of In and Zn; as well as compositions consisting essentially of In, Zn and one or more of Mg, Ca, Nb, Ta, B, Al, Ce, Ti and Zr.

**[0025]** To aid in interpretation of the claims that follow, the terms "semiconductive substrate" and "semiconductor substrate" are defined to mean any construction comprising semiconductive material, including, but not limited to, bulk semiconductive materials such as a semiconductive wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term "substrate" refers to any supporting structure, including, but not limited to, the semiconductive substrates described above.

## CLAIMS

1. A composition consisting essentially of In and Zn; with the Zn concentration being from about 0.5 weight% to about 3 weight%.
2. The composition of claim 1 being in the shape of a billet.
3. The composition of claim 1 being in the shape of a ribbon.
4. The composition of claim 1 being in the shape of a wire.
5. A composition consisting essentially of In, Zn, and one or more elements selected from the group consisting of Mg, Ca, Nb, Ta, B, Al, Ce, Ti and Zr; with the Zn concentration being from about 0.5 weight% to about 3 weight%.
6. The composition of claim 5 being in the shape of a billet.
7. The composition of claim 5 being in the shape of a ribbon.
8. The composition of claim 5 being in the shape of a wire.

9. The composition of claim 5 wherein a total concentration of the one or more elements is greater than 0 ppm and less than or equal to 1000 ppm.
10. The composition of claim 5 wherein a total concentration of the one or more elements is greater than 0 ppm and less than or equal to 500 ppm.
11. The composition of claim 5 wherein a total concentration of the one or more elements is greater than 0 ppm and less than or equal to 200 ppm.
12. The composition of claim 5 comprising Mg to a concentration greater than 0 ppm and less than or equal to 1000 ppm.
13. The composition of claim 5 comprising Mg to a concentration greater than 0 ppm and less than or equal to 500 ppm.
14. The composition of claim 5 comprising Mg to a concentration greater than 0 ppm and less than or equal to 200 ppm.

15. A composition consisting essentially of In, greater than 0 weight% Zn and less than or equal to about 2 weight% Zn, and from greater than 0 ppm to less than or equal to about 500 ppm Mg.

16. The composition of claim 15 comprising less than or equal to about 250 ppm Mg.

17. The composition of claim 15 comprising less than or equal to about 1 weight% Zn.

18. The composition of claim 17 comprising less than or equal to about 250 ppm Mg.

19. A semiconductor package, comprising:  
a semiconductor substrate;  
a heat spreader proximate the substrate; and  
a thermal interface material thermally connecting the substrate to  
the heat spreader; the thermal interface material consisting essentially of In and  
Zn; with the Zn concentration being from greater than 0 weight% to about 3  
weight%.

20. The composition of claim 19 wherein the Zn concentration is from  
greater than 0 weight% to about 2 weight%.

21. The composition of claim 19 wherein the Zn concentration is from about 0.5 weight% to about 2.2 weight%.

22. The composition of claim 19 wherein the Zn concentration is from about 0.5 weight% to about 1 weight%.

23. A semiconductor package, comprising:  
a semiconductor substrate;  
a heat spreader proximate the substrate; and  
a thermal interface material thermally connecting the substrate to the heat spreader; the thermal interface material consisting essentially of In, Zn, and one or more elements selected from the group consisting of Mg, Ca, Nb, Ta, B, Al, Ce, Ti and Zr; with the Zn concentration being from about 0.5 weight% to about 3 weight%.

24. The package of claim 23 wherein a total concentration of the one or more elements in the thermal interface material is greater than 0 ppm and less than or equal to 1000 ppm.

25. The package of claim 23 wherein a total concentration of the one or more elements in the thermal interface material is greater than 0 ppm and less than or equal to 500 ppm.
26. The package of claim 23 wherein a total concentration of the one or more elements in the thermal interface material is greater than 0 ppm and less than or equal to 200 ppm.
27. The package of claim 23 wherein the thermal interface material comprises Mg to a concentration greater than 0 ppm and less than or equal to 1000 ppm.
28. The package of claim 23 wherein the thermal interface material comprises Mg to a concentration greater than 0 ppm and less than or equal to 500 ppm.
29. The package of claim 23 wherein the thermal interface material comprises Mg to a concentration greater than 0 ppm and less than or equal to 200 ppm.

30. The package of claim 23 wherein the thermal interface material consists essentially of In, about 1 weight% Zn, and from greater than 0 ppm to less than or equal to about 500 ppm Mg.

31. The package of claim 23 wherein the thermal interface material consists essentially of In, about 1 weight% Zn, and from greater than 0 ppm to less than or equal to about 250 ppm Mg.

**AMENDED CLAIMS**

[received by the International Bureau on 18 September 2002 (18.09.02);  
original claims 1-31 replaced by new claims 1-16]

1. A composition consisting of In, Zn, and one or more elements selected from the group consisting of Ca, Nb, Ta, B, Ce, Ti and Zr; with the Zn concentration being from about 0.5 weight% to about 3 weight%.
  
2. The composition of claim 1 being in the shape of a billet.
  
3. The composition of claim 1 being in the shape of a ribbon.
  
4. The composition of claim 1 being in the shape of a wire.
  
5. The composition of claim 1 wherein a total concentration of the one or more elements is greater than 0 ppm and less than or equal to 1000 ppm.
  
6. The composition of claim 1 wherein a total concentration of the one or more elements is greater than 0 ppm and less than or equal to 500 ppm.
  
7. The composition of claim 1 wherein a total concentration of the one or more elements is greater than 0 ppm and less than or equal to 200 ppm.

8. A semiconductor package, comprising:

a semiconductor substrate comprising a silicon nitride surface;

a heat spreader proximate the substrate; and

a thermal interface material thermally connecting the substrate to the heat spreader; the thermal interface material being bonded to the silicon nitride surface; the thermal interface material consisting essentially of In, Zn, and one or more elements selected from the group consisting of Mg, Ca, Nb, Ta, B, Al, Ce, Ti and Zr; with the Zn concentration being from about 0.5 weight% to about 3 weight%.

9. The package of claim 8 wherein a total concentration of the one or more elements in the thermal interface material is greater than 0 ppm and less than or equal to 1000 ppm.

10. The package of claim 8 wherein a total concentration of the one or more elements in the thermal interface material is greater than 0 ppm and less than or equal to 500 ppm.

11. The package of claim 8 wherein a total concentration of the one or more elements in the thermal interface material is greater than 0 ppm and less than or equal to 200 ppm.

12. The package of claim 8 wherein the thermal interface material comprises Mg to a concentration greater than 0 ppm and less than or equal to 1000 ppm.

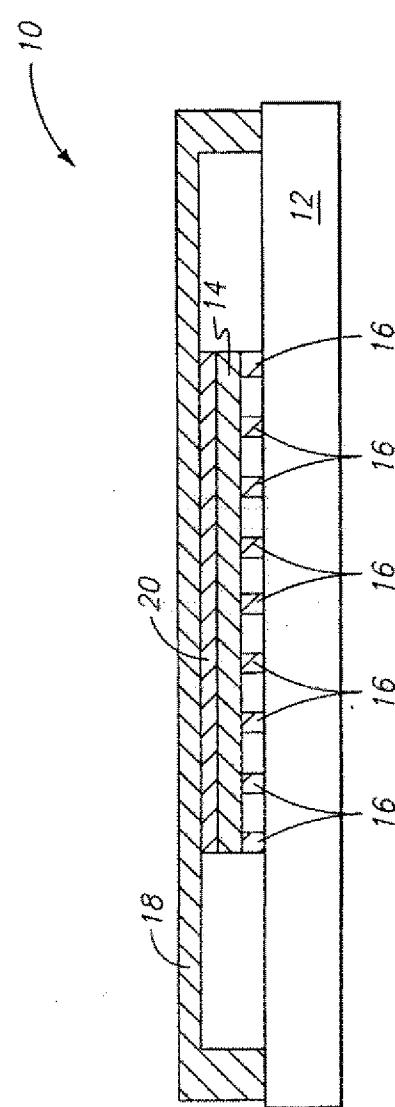
13. The package of claim 8 wherein the thermal interface material comprises Mg to a concentration greater than 0 ppm and less than or equal to 500 ppm.

14. The package of claim 8 wherein the thermal interface material comprises Mg to a concentration greater than 0 ppm and less than or equal to 200 ppm.

15. The package of claim 8 wherein the thermal interface material consists essentially of In, about 1 weight% Zn, and from greater than 0 ppm to less than or equal to about 500 ppm Mg.

16. The package of claim 8 wherein the thermal interface material consists essentially of In, about 1 weight% Zn, and from greater than 0 ppm to less than or equal to about 250 ppm Mg.

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US02/12821

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C22C 28/00

US CL : 420/555; 148/400; 257/276, 625, 675, 706, 717, 796

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 420/555; 148/400; 257/276, 625, 675, 706, 717, 796

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST, CAS ONLINE

search terms: indium, In, zinc, Zn, package

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 52061152 A (TOKE) 20 May, 1977, abstract.	1-18
Y		19-31

 Further documents are listed in the continuation of Box C.  See patent family annex.

• Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance		
"E" earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means		
"P" document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search 25 JUNE 2002	Date of mailing of the international search report 19 JUL 2002
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Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer SIKYIN IP Telephone No. (703)- 308-0661
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